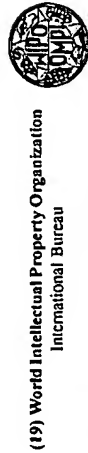


(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)



(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 March 2003 (06.03.2003) PCT WO 03/018466 A2

(51) International Patent Classification: C01B (74) Agents: KORDZIN, Kelly, K. et al.; Winstead Sechrest & Minick P.C., P.O. Box 50784, 1201 Main Street, Dallas, TX 75250-0784 (US).

(21) International Application Number: PCT/US02/06725 (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

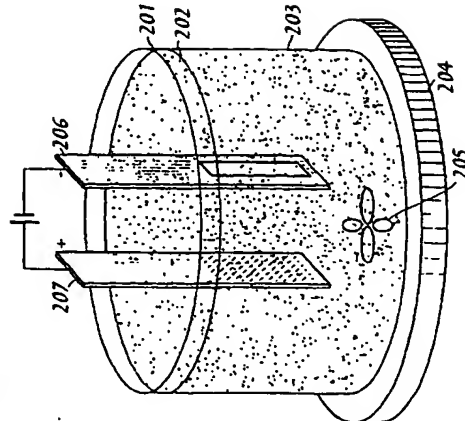
(71) Applicant: SI DIAMOND TECHNOLOGY, INC. (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors: MAO, Dongsheng; 12707 Pond Woods Road, # 1902, Austin, TX 78729 (US); LI, Yanjun; 9815 Copper Creek Drive, #404, Austin, TX 78729 (US); FINK, Richard; 3909 Hawkhead Drive, Austin, TX 78727 (US); GINSBERG, Valerie; 12422 Painted Bunton, Austin, TX 78726 (US); YANG, Mohabb; 10201 Spicewood Mesa, Austin, TX 78759 (US); THUESEN, Lefl; 1626 Sylvia Court, Round Rock, TX 78681 (US).

Published: without international search report and to be republished upon receipt of that report

(54) Title: CATALYST FOR CARBON NANOTUBE GROWTH

(57) Abstract: Nanoparticles (304, 705) are coated using thick-film techniques with a catalyst (202) to promote the growth of carbon nanotubes (410) thereon. In one example, alumina nanoparticles are coated with a copper catalyst. Such nanoparticles can be selectively deposited onto a substrate (206) to create a field emission cathode (702, 802), which can then be utilized within field emission devices (700).



WO 03/018466 A2

For two-letter codes and other abbreviations, refer to the "Guide to the Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BEST AVAILABLE COPY

CATALYST FOR CARBON NANOTUBE GROWTH

TECHNICAL FIELD

The present invention relates in general to carbon nanotubes, and in particular, to a process for growing carbon nanotubes.

BACKGROUND INFORMATION

Metal catalysts, such as nickel (Ni), cobalt (Co), iron (Fe), and their alloys, have been extensively investigated for carbon nanotube growth by chemical vapor deposition (CVD). A typical means of growing carbon nanotubes (CNTs) on the surface of a substrate is to deposit a thin film catalyst onto the surface. However, the thickness of catalyst is critical to the CVD grown CNTs in terms of their density, diameter, and length. Moreover, with Ni, Co, and Fe catalysts, it is difficult to control the diameter and density of CNTs due to their relatively high deposition rates and thickness sensitivity. On the other hand, field emission properties of CNTs are strongly dependent on their distributed density and aspect ratio. Thus, to control the growth of CNTs for a variety of applications, more types of catalyst and alloy need to be developed.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 illustrates a system for electroless plating;

FIGURE 2 illustrates a system for implementing a method in accordance with the present invention;

FIGURES 3A-3F illustrate a deposition process configured in accordance with the present invention;

FIGURES 4A-4G illustrate a process in accordance with the present invention;

FIGURE 5 illustrates images of a phosphor screen showing emission from cathodes configured in accordance with the present invention;

FIGURE 6 illustrates I-V characteristics of a carbon nanotube cathode prepared in accordance with the present invention;

FIGURE 7 illustrates a display device configured in accordance with the present invention;

FIGURE 8 illustrates a CRT configured in accordance with the present invention; and

FIGURE 9 illustrates a data processing system configured in accordance with the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

Beside nickel, cobalt, iron and their alloys, copper (Cu) as catalyst for CNT growth has been investigated. It has been found that CNTs can be grown with copper by a CVD technique, and demonstrate very good field emission properties. The copper catalyst can be used to grow thinner CNTs to obtain a relatively high aspect ratio for field emission applications. Moreover, the lower growth rate with copper than with nickel is strongly dependent on the deposition time to provide a way for controlling the length or thickness of CNTs.

The present invention deposits a thin film catalyst using thick-film techniques. Thus, one can deposit a preferred amount of catalyst using inexpensive processes. Other means of preparing a copper thin film catalyst may be employed, such as evaporating, sputtering, and other physical vapor deposition coating techniques, but thickness sensitivity still remains so that it is relatively hard to control the growth of CNTs to meet field emission application. Therefore, copper thin film coated on small particles is used for CVD deposition.

The method uses a three-step process.

Step 1: Coating a metal catalyst layer on small particles.

Referring to FIGURE 1, an electroless plating bath 100 is used to deposit a catalyst film onto nanoparticles. The size of the nanoparticles ranges from several nanometers to several hundred nanometers. The average size may be about 100 nanometers (about 0.1 micron). The nanoparticles may have many different shapes. One example of such nanoparticles is alumina (Al_2O_3), but other materials can be used for these particles. These particles can be insulating, semiconducting or conducting. The particles are compatible with

the bath chemicals (acids and bases) and able to withstand the temperatures for growing carbon films (range from 500°C to 900°C) in hydrogen and hydrocarbon atmospheres.

The metal film (e.g., Cu, Ag, Co, Ni, Fe) on the particles that are coated with the electroless plating bath 100 is the catalyst for carbon nanotube growth. Alloys of these metals may also be used. Multiple layers of these metals may also be used. Other means of coating the particles with the metal films may be used, such as plating with electrodes, spraying, evaporating, sputtering, and other physical vapor deposition coating techniques.

The bath used to coat the particles with Cu may be an electroless plating bath for coating Cu, containing water and the following chemicals:

1. Cu salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).
2. Promoter to dissolve the Cu salt in the solution ($\text{KNa}_3\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$). Concentration 80-100 grams per liter.
3. Solution to slow the reaction ($\text{NH}_4 \cdot \text{H}_2\text{O}$, 25%). Concentration 120ml per liter.
4. Balancing agent (NaOH). This material is used to control the pH value of the solution. The amount of this material used is that needed to achieve a pH of 8-10 of the plating solution.

The Cu ions will be produced at room temperature at this solution. The pH of the solution is important and is to be controlled before and during the reaction. In this solution above, the pH value is 12-14. It may be necessary to add NaOH during the plating process to control the pH of the solution. The details of this plating bath solution can be varied.

After the bath is prepared, the particles are added to the solution 109. The particles are added quickly while the solution 109 is being stirred with stir and motor 110. A thermometer 107 may be used to measure the temperature of the water 103, which is contained within beaker 102 having an insulating coating. A lid 105 may be placed over beaker 102. Additionally, a heater plate with a magnetic stirring motor 101 is used with a stirring rod 106 within the holder 104 to support the beaker 108. The amount of particles (weight) is determined by the desired thickness of the Cu coating on the particles. For one liter of the above solution, 5-10 grams of the alumina powder (particles) are added to the solution 109. If more Cu is desired, a less amount of particles is added. If less metal of the

particles is desired, more particles are added. The typical time of reaction is about 5-10 minutes. Longer times may not effect the results greatly. During reaction, much gas is evolved from the solution. The powder is white at the beginning and turns to black gradually. At the end of the reaction, little or no gas is evolved from the solution.

After reaction/deposition of metal, the reaction beaker 108 holding the bath and powder may be taken out of the water bath 103 and allowed to cool down to room temperature. After several hours, the particles will collect at the bottom of the beaker 108 and allow one to decant the solution 109 from the powder. Water may be added carefully to the powder in the beaker 108 to wash the powder. This may be done several times, each time being careful to not disturb the powder. Washing dilutes the concentration of the Cu bath still remaining on the powder after the reaction. The powder can be removed and dried in a furnace (not shown) at about 60°C-100°C. Other techniques may be used to wash and recover the particles. Filters may be used or centrifuges or other common laboratory techniques to recover the particles.

The result is that the particles are coated with a thin layer of catalytic film. This film may not be necessarily uniform on each particle or uniform from particle to particle. The film thickness on a particle can range from 1nm to 100nm because different shapes, edges, or tips of the particles may have more surface energy and promote more deposition of the catalyst than other less reactive areas of a particle. This has several advantages:

1. It provides a wide range of catalytic activity for the metal coated particles. Some particles may be more reactive than others for a particular process (such as growing carbon nanotubes as will be described later). If the process changes, then other particles may be reactive.
 2. This provides a large surface area for later reactions. The surface area of a layer of particles may be orders of magnitude larger than a well polished surface.
- Step 2. Depositing the catalytic particles on a substrate or surface.

Once the particles are activated with a catalytic layer, these catalytic particles can be deposited onto a substrate for certain reactions. The catalytic particles may be used to assist in growing a carbon nanotube film on a substrate. Other applications may not require this.

To deposit the catalytic particles onto a surface, many techniques have been developed. These include electrophoresis, spraying (see FIGURES 3A-3F), painting, printing (including ink jet), and immersing (dunking) a substrate in a solution of catalytic particles. Other processes may be used for applying the particles to a substrate.

Referring to FIGURES 2 and 4A-4G, one method of depositing the particles is by using electrophoresis (EP) techniques. In this method, the particles 202 are suspended in a bath 203 containing a solvent (e.g., isopropyl alcohol) and particle surface charge promoters such as $Mg(NO_3)_2 \cdot 6H_2O$ in order to improve the deposition rate. The concentration of the $Mg(NO_3)_2 \cdot 6H_2O$ may be on the order of 10^{-3} to 10^{-2} moles/liter. The technique is much like a plating process, except particles 202 are coated onto the surface 206 instead of atoms of materials. EP techniques are commonly used for depositing particles of phosphor onto conducting anode faceplates used in cathode ray tubes (televisions). The substrate 206 is placed in the solution 203 opposite an electrode 207 that is also placed in the solution 203. The electrode 207 may be metal or graphite and could be a mesh or screen and not a solid sheet. The gap between the electrode 207 and the substrate 206 may be on the order of 2cm - 4cm. The electrode 207 and substrate 206 are about the same size, but it is not necessary. The voltage between the anode 207 and substrate 206 is on the order of 400V, with the electrode 207 being positive and the substrate surface 206 being negative with respect to each other. The solution 203 may be stirred constantly, using a stirring bar 205 and magnetic agitator 204, to disperse the particles 202 in the solution 203 uniformly. After the deposition of particles 202, the substrate 206 is dried in a furnace at 50C - 100C in air.

Figure 4 shows this process through completion of the deposition. FIGURE 4A shows the substrate 206 having a base insulating substrate 401. In FIGURE 4B, a conducting layer 402 is added on top of the insulating substrate 401. The conducting layer may be made patterned. In FIGURE 4C, a photoresist layer 403 is placed on top of the conducting layer 402. In FIGURE 4D, the photoresist layer is patterned using typical techniques. It is this version of the substrate 206 which may be immersed in the EP solution 203, as illustrated

in FIGURE 2, to deposit the particles 202 thereon. In FIGURE 4E, most of the particles may be deposited onto the conducting layer 402, but some may also adhere to the photoresist layer 403. After the process in FIGURE 2 is completed and the substrate 206 is removed, in FIGURE 4F, the photoresist layer 403 is removed, stripping the particles away that were deposited on the photoresist layer 403, and not where this layer exposed the conducting layer 402 to the electrophoretic bath 203.

Step 3: Deposition of the carbon nanotube film

Referring to FIGURE 4G, the substrate 206 with catalytic particle coating 202 is then mounted into a reactor (not shown) for depositing the carbon nanotubes 410. The reactor used may be a quartz tube furnace that operates at high temperatures and with a controlled atmosphere inside the tube. The process may be a thermal CVD process.

The substrate 206 is placed at the cold end of the reactor. After the substrate 206 is placed in the reactor, the reactor is closed off to room atmosphere and pumped down to 10^{-2} Torr using standard rough pumps. Then the reactor is back-filled with nitrogen gas to a pressure of 100 Torr. Nitrogen continues to flow at about 100scm but the pressure is regulated with a throttle valve above the pump. Then the substrate 206 is pushed into the center of the furnace where it will heat up to high temperature. After the substrate 206 is pushed into the furnace, the nitrogen gas is switched off, and hydrogen gas is switched on, also at 100 scm flow rate. The temperature can be in a range from 450°C to 750°C. The substrate 206 sits in this environment of flowing hydrogen for about 10-30 minutes to allow the temperature of the substrate 206 to come to equilibrium with its new environment. Then the hydrogen is switched off and acetalene (C_2H_2) gas flow is turned on at a flow rate of 20-50 scm. The pressure remains at 100 Torr. The time of this period is 5-60 minutes. After this carbon growth period, the acetalene gas flow is turned off and the nitrogen gas flow is turned on at a flow rate of 100scm. At the same time the substrate 206 is pulled from the hot zone of the reactor to the cold zone and allowed to cool down to near room temperature. After about 10 minutes, the reactor is again evacuated and then vented to air. When the pressure reaches 1 atmosphere, the reactor is opened and the substrate 206 is removed, inspected and tested.

These parameters can be varied. Other hydrocarbon gasses can be used. Combinations of hydrocarbon gasses with each other and with hydrogen or other gasses may also be used. Carbon monoxide gas may also be used. Other forms of CVD deposition may also be used. Examples such as RF, microwave and DC plasma generation and hot wire filaments CVD are well-known methods for growing CNT films.

In summary, copper coated catalytic particles 202 are used for carbon film 410 growth. It was found that thinner CNTs with a relatively high aspect ratio were prepared. This catalyst provides a way to controllably grow CNTs by CVD. The copper coated particles also allow the use of thick film techniques to deposit the thin film catalysts on substrates for CVD carbon growth.

Substrates can be of different materials such as silicon, ceramic or glass. The catalyst can be applied in patterns as well as blanket coats on the substrates. The carbon films have then been deposited and the cathodes have emitted with good definition in the patterned areas.

FIGURES 3A-3F illustrate an alternative method for depositing the nanoparticles onto the substrate. An insulating substrate 301 is provided in FIGURE 3A. In FIGURE 3B, a conducting layer 302 is added to the substrate 301. In FIGURE 3C, a photoresist or hard mask layer with a predetermined pattern (e.g., holes) is added on top of the conducting layer 302. In FIGURE 3D, the deposition of nanoparticles 304 is performed by some other method, such as spraying. The solvent used with particles 304 is evaporated and not shown in FIGURE 3D. This solvent should not interfere with the hard mask. In FIGURE 3E, the mask 303 is removed, leaving the particles 304 on the surface of the conducting layer 302 only in the areas that the mask 303 did not cover. In FIGURE 3F, carbon nanotube fibers 305 are grown on the particles 304, similarly as described above.

FIGURE 5 illustrates images of a phosphor screen captured during testing of cathodes that are prepared with copper catalyst and copper catalyst under CVD growth conditions. The image on the left shows the cathode with copper catalyst at 3.7 μm and 15 mA/cm². On the right, the cathode with nickel catalyst is at 5 V/ μm and 6 mA/cm². The area of the cathode is about 2.5 cm².

Cathodes on silicon are tested by mounting them with a phosphor screen in a diode configuration with a gap of about 0.5 mm. The test assembly is placed in a vacuum chamber and pumped to 10⁻⁷ Torr. The electrical properties of the cathode are then measured by applying a negative, pulsed voltage to the cathode and holding the anode at ground potential and measuring the current at the anode. A pulsed voltage is used to prevent damage to the phosphor screen at the high current levels. Tests on the cathodes show threshold extraction fields of about 2 V/ μm , and current densities reaching near 15 mA/cm² at an electric field strength of around 3.7 V/ μm . I-V curves of field emission from CNTs prepared from copper and nickel coated particles are shown in FIGURE 6. The higher current at low fields from CNTs grown from copper catalyst than that of nickel is mainly attributed to a smaller diameter of CNTs resulting in a larger aspect ratio.

Referring to FIGURE 7, there is illustrated a field emission display device 700 utilizing a cathode 702 with carbon nanotubes, such as those produced in accordance with the present invention. Cathode 702 includes an insulating substrate 703 with a conducting layer 704 thereon. On the conducting layer 704 are nanoparticles 705 with carbon nanotubes grown thereon, which will emit electrons as a result of the application of the fixed and variable electric fields shown. The electrons will be emitted towards anode 700, which includes anode 701 which includes glass substrate 706 with a transparent conductor 707 and a phosphor material 708. Grid 709 may optionally be included.

Referring to FIGURE 8, the cathode produced in accordance with the present invention may be utilized as the cathode for a field emission electron gun 802 within a cathode ray tube 801. Other circuitry that might be utilized to deflect and focus the electron beam produced by the cathode 802 is not shown for the sake of simplicity.

A representative hardware environment for practicing the present invention is depicted in FIGURE 9, which illustrates an exemplary hardware configuration of data processing system 913 in accordance with the subject invention having central processing unit (CPU) 910, such as a conventional microprocessor, and a number of other units interconnected via system bus 912. Data processing system 913 includes random access memory (RAM) 914, read only memory (ROM) 916, and input/output (I/O) adapter 918 for connecting peripheral devices such as disk units 920 and tape drives 940 to bus 912, user

WHAT IS CLAIMED IS:

1. A method comprising the steps of:
coating nanoparticles with a catalyst;
depositing the nanoparticles coated with the catalyst onto a substrate; and
growing carbon nanotubes on the nanoparticles.
2. The method as recited in claim 1, wherein the catalyst has a property that promotes carbon nanotube growth there upon.
3. The method as recited in claim 2, wherein the coating step uses an electroless plating bath process to coat the catalyst onto the nanoparticles.
4. The method as recited in claim 3, wherein the catalyst is a metal.
5. The method as recited in claim 4, wherein the metal is copper.
6. The method as recited in claim 4, wherein the metal is nickel.
7. The method as recited in claim 4, wherein the metal is cobalt.
8. The method as recited in claim 4, wherein the metal is iron.
9. The method as recited in claim 4, wherein the metal is silver.

10. The method as recited in claim 1, wherein the catalyst is copper.

11. The method as recited in claim 3, wherein coating of the nanoparticles takes place in a bath comprising:

- a compound containing the catalyst;
- a promoter to dissolve the compound in a bath solution;
- a reaction slowing agent; and
- a pH balancing agent.

12. The method as recited in claim 11, wherein the electroless plating bath process further comprises the steps of:

- decanting a remaining liquid from the bath, leaving the coated nanoparticles; and
- drying the coated nanoparticles.

13. The method as recited in claim 2, wherein the depositing step deposits the nanoparticles coated with the catalyst in a predetermined pattern onto the substrate.

14. The method as recited in claim 2, wherein the substrate is prepared by depositing a conducting layer onto an insulating layer.

15. The method as recited in claim 2, wherein the depositing step uses an electrophoretic process to deposit the nanoparticles coated with the catalyst in a predetermined pattern.

16. The method as recited in claim 2, wherein the depositing step further comprises the steps of:

- depositing a mask layer onto the substrate, the mask layer having a predetermined pattern;

depositing the nanoparticles coated with the catalyst onto the substrate and mask layer; and
removing the mask layer leaving the substrate with the nanoparticles with the catalyst deposited thereon in the predetermined pattern.

17. The method as recited in claim 2, further comprising the steps of:

- positioning a screen having a phosphor thereon a predetermined distance from the substrate, the substrate including the coated nanoparticles with carbon nanotubes grown thereon; and

positioning circuitry in proximity to the substrate, the circuitry operable for creating an electric field to promote field emission of electrons from the carbon nanotubes grown onto the coated nanoparticles towards the screen.

18. An apparatus comprising:

- a substrate;
- nanoparticles deposited on the substrate, wherein the nanoparticles are coated with copper; and
- carbon nanotubes grown on the copper coated nanoparticles.

19. The apparatus as recited in claim 18, wherein the substrate includes a conducting layer on an insulating base, wherein the copper coated nanoparticles are deposited on the conducting layer.

20. The apparatus as recited in claim 18, further comprising:

- circuitry for creating an electric field to promote field emission of electrons from the carbon nanotubes.

21. The apparatus as recited in claim 20, further comprising:

- a phosphor screen positioned a distance from the substrate.

22. A field emission apparatus comprising:

a cathode including a conducting layer on a substrate; and catalyst coated nanoparticles deposited on the conducting layer in a predetermined pattern, wherein carbon nanotubes are deposited on the catalyst coated nanoparticles.

23. The apparatus as recited in claim 22, further comprising:
circuitry for creating an electric field to promote field emission of electrons from the carbon nanotubes.

24. The apparatus as recited in claim 23, further comprising:
a phosphor screen positioned a distance from the cathode.

1/7

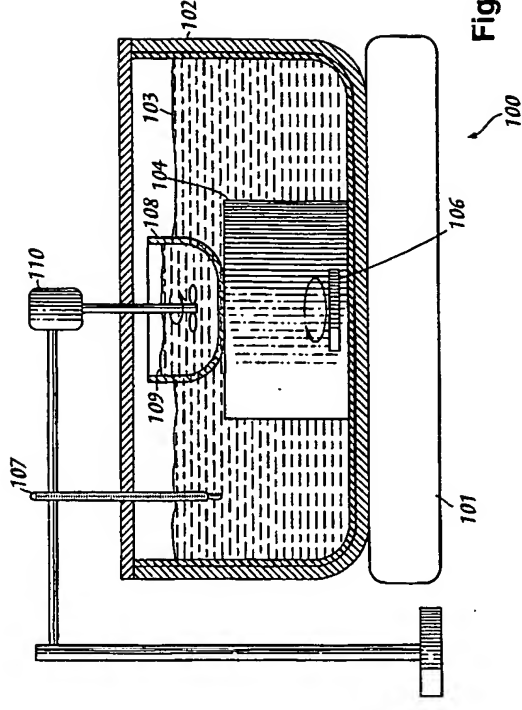


Fig. 1

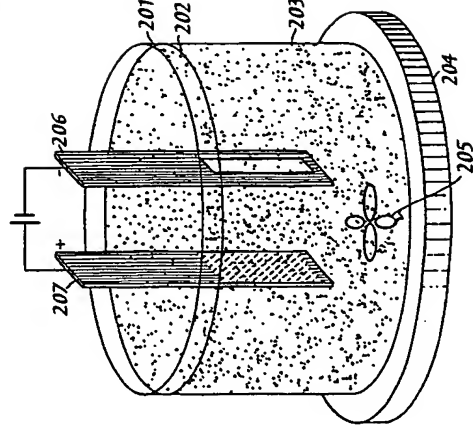
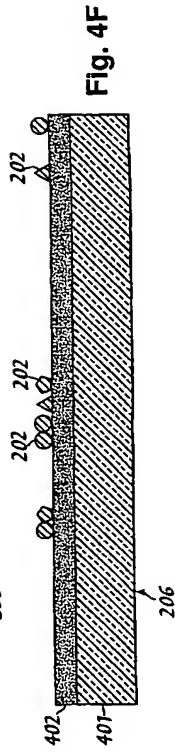
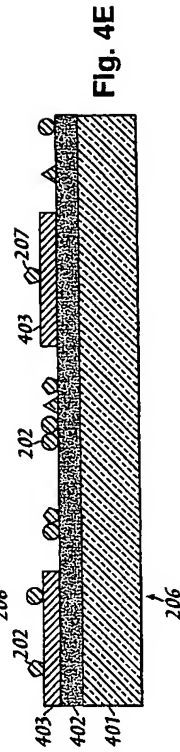
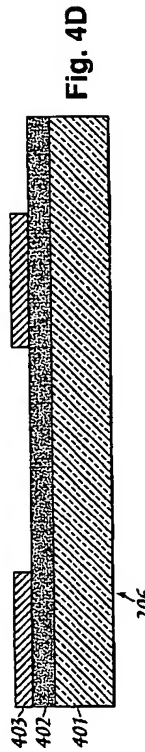
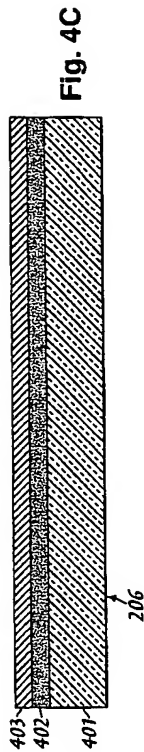
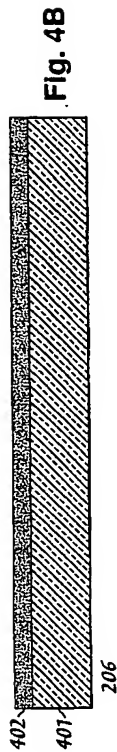
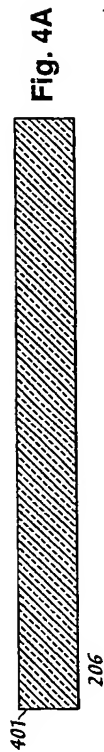
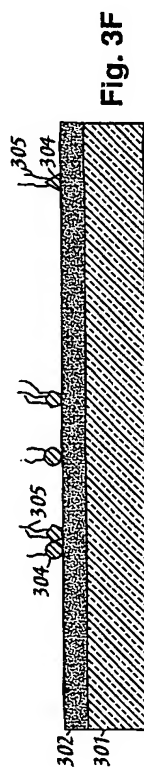
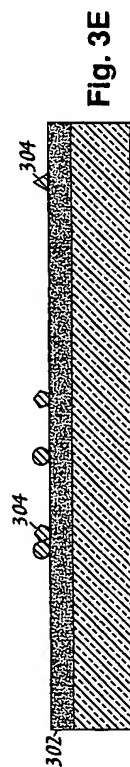
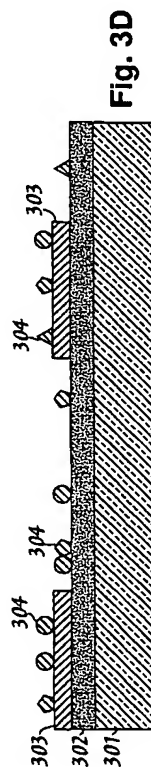
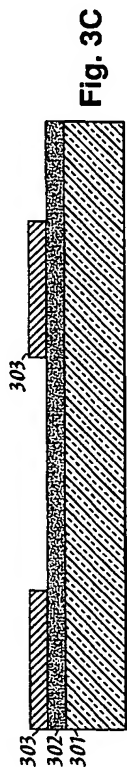
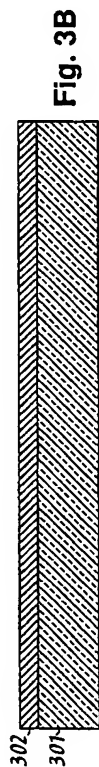


Fig. 2



4/7

5/7

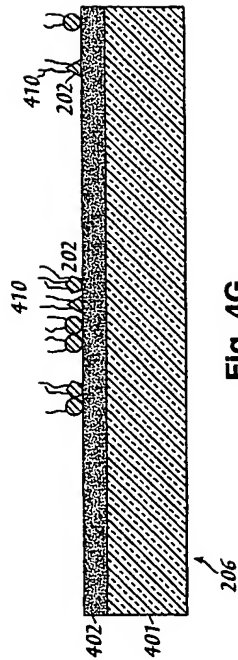


Fig. 4G

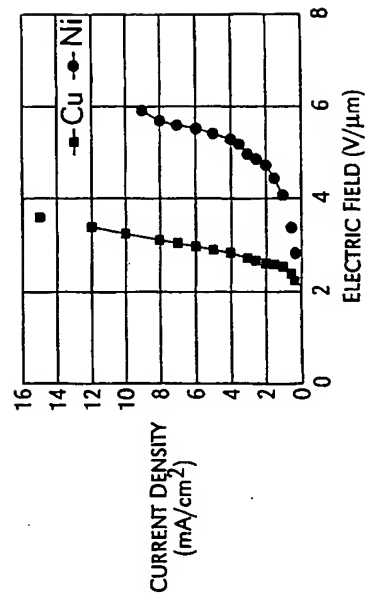


Fig. 6

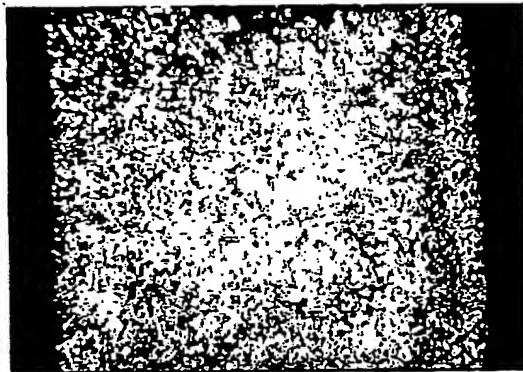


Fig. 5



6/7

7/7

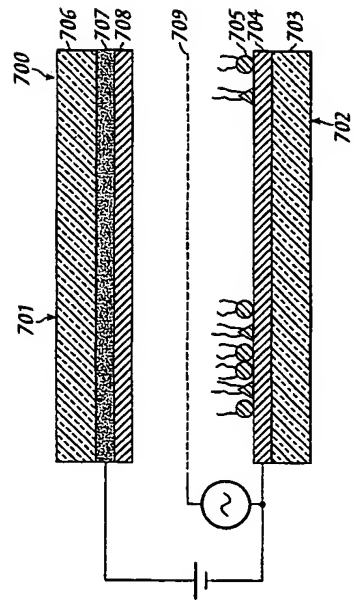


Fig. 7

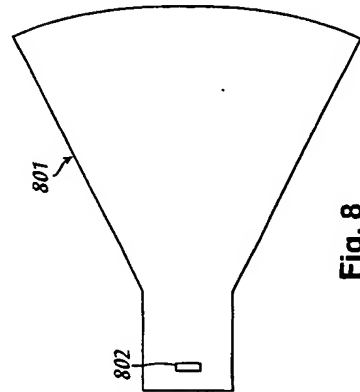


Fig. 8

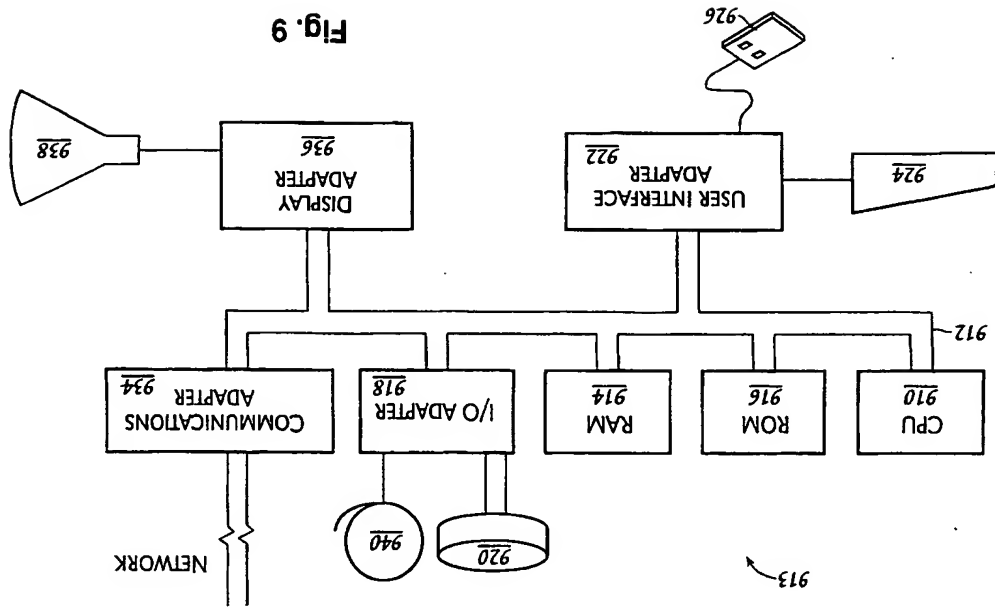


Fig. 9

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)



(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 March 2003 (06.03.2003)

PCT

(10) International Publication Number
WO 2003/018466 A3

(51) International Patent Classification: B05D 5/12, 7/24, 7/18, C01B 31/00, H01J 9/02, 29/04
(74) Agents: KORDZIK, Kelly, K. et al.; Winstead Sechrest & Minick P.C., P.O. Box 50784, 1201 Main Street, Dallas, TX 75250-0784 (US).

(21) International Application Number: PCT/US2002/026725

(22) International Filing Date: 22 August 2002 (22.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 24 August 2001 (24.08.2001) US 60314,870
20 August 2002 (20.08.2002) US 10223,815

(71) Applicant: NANO-PROPRIETARY, INC. [US/US]; 3006 Longhorn Boulevard, Suite 107, Austin, TX 78701 (US).

(72) Inventors: MAO, Dongheng; 12707 Pond Woods Road, # 1902, Austin, TX 78729 (US); LI, Yunjun; 9815 Cooper Creek Drive, #404, Austin, TX 78729 (US); RINK, Richard; 3909 Hawkhead Drive, Austin, TX 78727 (US); GINSBERG, Valerie; 12422 Painted Bunlin, Austin, TX 78726 (US); YANG, Mohshi; 10201 Spicewood Mesa, Austin, TX 78759 (US); THUESSEN, Lef; 1626 Sylvia Court, Round Rock, TX 78681 (US).

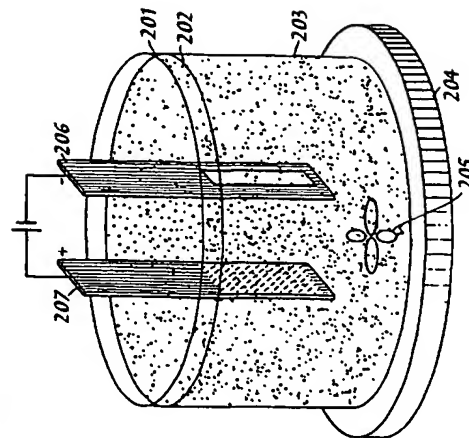
Published:
— with international search report

(88) Date of publication of the international search report: 4 March 2004

[Continued on next page]

(54) Title: CATALYST FOR CARBON NANOTUBE GROWTH

(57) Abstract: Nanoparticles (304, 705) are coated using thick-film techniques with a catalyst (202) to promote the growth of carbon nanotubes (410) thereon. In one example, alumina nanoparticles are coated with a copper catalyst. Such nanoparticles can be selectively deposited onto a substrate (206) to create a field emission cathode (702, 802), which can then be utilized within field emission devices (700).



WO 2003/018466 A3

For two-letter codes and other abbreviations, refer to the "Guide to the Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

INTERNATIONAL SEARCH REPORT		International application No.
A. CLASSIFICATION OF SUBJECT MATTER IPC Class. : B03D 5/12, 7/24, 17/18; C01B 31/00; H01J 9/02, 29/04 US CL : 427/77, 197, 198, 199, 217, 443.1, 903; 443/46, 31; 313/458, 467 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 427/77, 78, 180, 197, 198, 199, 212, 215, 217, 437, 438, 443.1, 903; 423/443B, 445B; 443/46, 31; 313/564, 458, 467		PCT/US02/26725
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Please See Continuation Sheet		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/1702 A1 (WILLIAM MARSH RICE UNIVERSITY) 30 March 2000	1 and 2
Y	US 5,453,297 A (DYB et al) 26 September 1995 (26.09.1995), abstract, column 4, lines 36-67, column 5-6, column 8, lines 1-24, column 9, lines 12-21, column 11, lines 64-67, and column 12, lines 1-10.	3-14 and 16-24
Y	US 6,325,809 B1 (Li et al) 04 December 2001 (04.12.2001), abstract and column 6, lines 41-51.	3-9, 11, and 12
Y	US 5,872,422 A (XU et al) 16 February 1999 (16.02.1999), abstract and column 5, lines 8-30.	5, 10, and 18-21
Y	US 2001/0033344 A1 (HARUTYUNYAN et al) 20 December 2001 (20.12.2001), abstract and page 4, paragraph [0038].	5, 10, and 18-21
Y	US 5,925,415 A (FRY et al) 20 July 1999 (20.07.1999), abstract, column 2, lines 56-59, and column 4, lines 1-60.	9
Y	US 6,339,381 B2 (LEE et al) 15 January 2002 (15.01.2002), abstract, Figures 1, 2A-2H, 3A-3C, and 5, column 1, lines 8-64, and column 4.	11 and 12
Y		13, 14, 16, 17, and 19-24
Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *B* earlier application of patent published on or after the international filing date *C* document which may show dates on priority claim(s) or which is cited to establish the publication date of another claim or other specific feature (as specified) *D* document referring to an oral disclosure, use, exhibition or other means *E* document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 08 November 2002 (06.11.2002)		
Name and mailing address of the ISA/US Searcher PCT Washington, D.C. 20541 Facsimile No. (703) 305-3230		
Date of mailing of the international search report 10 DEC 2002		
Authorized officer Shrive Beck Telephone No. (703) 308-0661		

Continuation of B. FIELDS SEARCHED Item 3:
 WEST electronic database for U.S. Patents and pre-grant publications, JPAB, EPAB, Derwent patent abstracts, and IBM technical disclosure bulletins
 search terms: nanotube, SWNT, CNT, MWNT, buckytube, fullerene tube, nanosparcels, catalyst, support, nickel, silver, copper, cobalt, iron, electron emissive, field emission, electrodes, electrophoresis, and variations and combinations thereof

BEST AVAILABLE COPY